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Incorporation of U and Th in Phosphatized Fossils

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Introduction: By understanding how actinides are incorporated in the minerals that fossilize bones, we hope to provide insight into the fate of these elements in surficial processes and possibly through diagenetic alteration after burial. This study took advantage of the 10-micron beam size at the X26A beam line to map major and trace elements compositions using x-ray fluorescence (XRF) and to determine the U oxidation states using fluorescence mode x-ray absorption near-edge spectroscopy (XANES).

Results: The analyses show dramatic differences in actinide behavior in three different fossil bones from three formations: the Jurassic Morrison Formation, the Cretaceous Cedar Mountain Formation and the Eocene Green River Formation. The Morrison Fm Glyptopsidae shell bone has high concentrations of U and low Th within the francolite of the fossilized bone, however the U and Th are both low abundance within the calcite that fills the Haversian canals (Fig. 1). U-XANES analyses on the Morrison francolite shows mixed oxidation states. The Cedar Mountain Fm bone (unidentified dinosaur sp.) is also francolite with high concentrations of U and low Th. Calcite fills the Haversian canals in the dinosaur bone, however the calcite has not been analyzed for trace elements. U-XANES analyses on the Cedar Mountain bone show solely U (IV). A francolite fish fossil from the Green River Fm has low U concentration but is highly enriched in Th (Fig. 2). U-XANES was not attempted on the Green River fish fossil due to the low abundance of U.

Conclusions: U has multiple oxidation states and is easily oxidized in surface environments. Studies show that in natural settings and in the lab U is not easily reduced even in very reducing fluids. Reduction appears to happen after adsorption to a surface and likely via microbial processes, although in some cases the mineral itself appears to control the oxidation state. The bone from the Morrison Fm seems to show a more complex history in that the U is mixed oxidation states. Perhaps later oxidizing fluids were responsible for causing some of the U in the bone to be oxidized. Alternatively, the oxidized U in the bone may be associated with organic material and was incorporated as U(VI) while U(IV) was incorporated in the apatite. Lanzirotti et al. [1] found that all of the U in a phosphatized coprolite was U(VI). They further showed that where U was high in the coprolite, Sr was low suggesting a dilution of the francolite possibly by organic material in which the U is complexed. The Green River Fm is known for a variety of unusual minerals and the waters, at least towards the upper part of the formation, were highly alkaline. While Th is generally considered a highly immobile element, it is known to be soluble in alkaline lakes [2] and can strongly complex with organic ligands, which may explain why Th is concentrated in the fish fossil. Perhaps more interesting is the low concentration of U in this francolite.

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References:

[1] A. Lanzirotti, M. Becker, G.N. Hanson and S.R. Sutton, "Uranium Behavior in Jurassic Fish Coprolites: Combined Microbeam Synchrotron X-Ray Fluorescence, Diffraction and XANES Analysis," Brookhaven National Laboratory, Upton, NY, BNL Report No. 52615 (2001).

[2] H.J. Simpson, et al., "Radionuclides in Mono Lake, California," Science, 31, no. 7, 512-514 (1982).

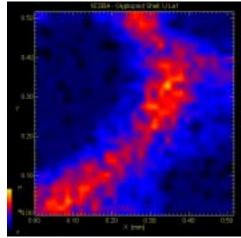


Figure 1: The XRF map the Gyptopsidae shell (curved feature), U concentrations are high in the bone phosphate and low in the calcite filled Haversian canals.

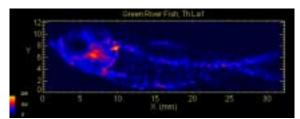


Figure 2: The XRF map of the Green River Fm fish fossil shows Th is concentrated in the bones of the entire fish. Concentration contours reflect the thickness of the mineral.